

Soft spin waves in the low temperature thermodynamics of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

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Abstract

We present a detailed magnetothermal study of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, a perovskite manganite in which an insulator-metal transition can be driven by magnetic field, but also by pressure, visible light, x-rays, or high currents. We find that the field-induced transition is associated with an enormous release of energy which accounts for its strong irreversibility. In the ferromagnetic metallic state, specific heat and magnetization measurements indicate a much smaller spin wave stiffness than that seen in any other manganite, which we attribute to spin waves among the ferromagnetically ordered Pr moments. The coupling between the Pr and Mn spins may also provide a basis for understanding the low temperature phase diagram of this most unusual manganite.

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The rare earth perovskite manganites ($R_{1-x}A_x\text{MnO}_3$) are associated with a wide variety of fascinating physics due to the strong coupling between their electronic, magnetic and lattice degrees of freedom. Phenomena observed in these materials include “colossal” magnetoresistance, real-space charge ordering, electronic phase separation, and a diverse variety of magnetoelectronic ground states [1]. Although this entire class of materials displays unusual behavior, one material, $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO), has been shown to display a particularly rich set of phenomena. Like several other manganites, the resistivity of PCMO is reduced by orders of magnitude in a magnetic field due to an irreversible transition from an insulating antiferromagnetic to a metallic ferromagnetic state [2–6]. What sets PCMO apart from the other manganites is that the metastable insulating state also can be driven metallic by the application of light [7,8], pressure [9], x-rays [10], or a high current [11]. Despite the strong recent interest in this wide range of unique phenomena in PCMO, there has been no clear understanding of why this particular manganite is so different from the others.

We have performed a detailed study of the low temperature magnetothermal properties of PCMO. We find that there is an enormous release of heat at the field-induced insulator to metal transition at low temperatures, which explains the complete irreversibility of the transition. In the ferromagnetic (FM) state at low temperatures, our specific heat and magnetization measurements indicate a ferromagnetic spin wave stiffness which is far below that seen in other conducting manganites. The data can be explained most easily as a result of ferromagnetism among the moments associated with the Pr ions, suggesting that the Pr magnetism is crucial to understanding the unusual low temperature properties of this material.

We studied both a ceramic sample of PCMO, synthesized by a standard solid state technique, and a single crystal grown in a floating zone mirror furnace. Both samples were judged to be single phase from x-ray diffraction studies. The cation concentration ratio, as measured by plasma atomic emission spectroscopy, was also consistent with the nominal concentration. While we show only results from the single crystal, data from the two samples were qualitatively and quantitatively consistent in all of the studied properties, and both had

low temperature phase diagrams (including a regime of field-induced ferromagnetic metallic phase) consistent with previously published studies of PCMO [5]. Magnetization was measured in a Quantum Design SQUID magnetometer, and specific heat was measured by a semiadiabatic heat pulse technique calibrated against a copper standard. Magnetocaloric measurements were made by temperature-controlling the calorimeter at a few degrees above the surrounding cryostat temperature while the field was swept. We then measured the input power required to maintain constant temperature during the field sweep and attributed changes in the input power to magnetocaloric effects.

The field-temperature phase diagram of PCMO is shown in the inset of figure 1 based on earlier measurements [5]. Upon cooling in zero field, PCMO first undergoes a charge-ordering transition at $T_{co} \sim 230$ K. Upon further cooling, the Mn spins order first into a pseudo-CE type antiferromagnetic state at $T_{AF} \sim 150$ K, and then into a canted antiferromagnetic (CAFM) state at a lower temperature T_{CAFM} [3]. This low field phase is quite complex due to the incommensurability of the charge order with the 30% Ca doping, and the resultant disorder leads to both spin-glass-like behavior [3,5] and electronic phase separation [8]. Application of a sufficiently high magnetic field at low temperatures induces a first order transition from the CAFM phase to a conducting FM state, and there is a strong hysteresis associated with this transition (the hatched region in the inset indicates where the state is history-dependent). For $T \lesssim 60$ K, the transition is completely irreversible so that if the material undergoes the field-induced FM transition it remains in a FM conducting state until the temperature is raised above 60 K. In figure 1 we demonstrate this irreversibility by plotting the magnetization vs. field after zero-field-cooling to $T = 10$ K and then sweeping the field up and down $0 \rightarrow 7$ T $\rightarrow -7$ T $\rightarrow 7$ T. The reduced moment during the initial sweep up in field for $H < 4$ T corresponds to the magnetization of the canted antiferromagnetic phase, and the rise in magnetization during that sweep at ~ 4 T corresponds to the phase transition. As seen in the figure, the magnetization maintains its ferromagnetic nature during all subsequent field sweeps.

Since the field-induced phase transition is highly irreversible and therefore first order, one

expects an associated release of heat which should be observed in our magnetocaloric measurements. In figure 2 we show the raw data of a magnetocaloric measurement, plotting the power input from the temperature controller (P) vs. magnetic field after zero-field-cooling as the field is changed from $0 \rightarrow 9$ T, 9 T \rightarrow -9 T, and -9 T \rightarrow 9 T. For $H \lesssim 1$ T we see small rises and falls in $P(H)$ during the initial sweep up in field. We attribute these reproducible features to heat release associated with the spin-glass-like character of the zero-field-cooled CAFM state [3,4], i.e. irreversible relaxation of the spin configuration during the initial field sweep [12,13] (a more detailed treatment of this behavior will be included in a future paper [14]). The most prominent feature in the magnetocaloric data, however, is the large negative peak in $P(H)$ during the initial field sweep. This peak corresponds to a reduction in the heat required from the temperature controller to maintain constant temperature, and we attribute this reduction to the heat released at the CAFM-FM transition. Note that there is no similar peak observed in subsequent sweeps of the magnetic field, which is consistent with the irreversibility of the transition.

The integrated magnitude of the peak in $P(H)$, $Q = \int (P/(\frac{dH}{dt}))dH$, is extraordinarily large at low temperatures - about 15 ± 1 J/mole. Within our resolution, Q is independent of both the sweep rate between 6 G/sec and 24 G/sec and the temperature for $T \lesssim 40$ K, but Q gradually decreases for higher temperatures [14]. Comparing the magnitude of Q to $\int C(T)dT$, one finds that the heat release at the transition is sufficient to raise the temperature of a perfectly thermally isolated sample from 5 to 17.5 K, i.e. by more than a factor of 3. Indeed, as can be seen in the inset to figure 2, when we simply sweep the field on our 0.22 gram sample on the calorimeter, the temperature of the calorimeter rises from 5 to 11 K. The magnitude of Q can be understood as a release of the Zeeman energy associated with the CAFM phase relative to that in the FM phase. This can be calculated from our measured value of $M(H)$ as $\int H dM$ over the field range of the transition which is 10 ± 1 J/mole for $T \lesssim 40$ K, in reasonable agreement with the measured values of Q [14]. The large magnitude of Q relative to the specific heat explains the complete irreversibility of the transition at low temperatures, since there is no corresponding energetic advantage

to the CAFM phase at low fields which would drive the reversal of the transition.

We measured the specific heat as a function of temperature, $C(T)$, at 0, 3, 6, and 9 tesla after cooling at those fields and at 0 and 3 tesla in the FM state (induced by raising the field temporarily to 9 T after reaching low temperatures). As shown in figure 3 we find that we can fit the temperature dependence in the FM state with the simple form $C(T) = \beta T^3 + \delta T^{3/2}$ where the two terms correspond to the lattice specific heat and the specific heat associated with ferromagnetic spin waves respectively. While we cannot rule out the possibility of a contribution to the specific heat which is linear in temperature (such as would arise from either free electrons or a spin glass state), we find that $C_{mag} = C(T) - \beta T^3$ has a power law temperature dependence with an exponent of almost exactly 1.5 as shown in the log-log plot in the inset to figure 3. Our fitted values of β vary with field by only a few percent, while $\delta(H)$ varies by 65% implying that the field dependence of the specific heat originates almost entirely in the magnetic component. We directly measured the field-dependence of the specific heat, $C(H)$ by zero-field cooling the sample and then measuring the specific heat every 0.25 T while sweeping the field from $0 \rightarrow 9 \text{ T} \rightarrow -9 \text{ T} \rightarrow 9 \text{ T}$ as shown in figure 4. During the initial sweep up in field, there is a sharp drop in $C(H)$ at about 4 T corresponding to the CAFM \rightarrow FM phase transition. On all subsequent sweeps, $C(H)$ is quite smooth and monotonically decreases as the magnitude of the applied field increases. Since the fits to $C(T)$ indicate that the lattice contribution to the specific heat (βT^3) is almost field-independent, we fit $C(H)$ in the FM state to a Heisenberg spin wave model as shown by the solid line in figure 4 [16]:

$$C(H) = A + \frac{V_{mole} k_B^{5/2} T^{3/2}}{4\pi^2 D^{3/2}} \int_{g\mu_B H/k_B T}^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} \sqrt{x - \frac{g\mu_B H}{k_B T}} dx \quad (1)$$

where V_{mole} is the molar volume and the only two fitting constants A and D are an offset to account for the lattice contributions and the stiffness constant of the spin wave spectrum respectively [17]. While such a form can also fit $C(H)$ in other ferromagnetic manganites, the magnitude of the field-induced suppression of $C(H)$ is 15 times larger in PCMO than in the other ferromagnetic manganites such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (shown as dashed line in

figure 4) and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [15]. This larger suppression of C in a field implies that the magnetic specific heat is much larger in PCMO than in the other materials and consequently that the spin wave spectrum is much softer. The fit to $C(H)$ of PCMO yields a value of $D = 28.0 \pm 0.3 \text{ meV-}\text{\AA}^2$. This is a factor of 5-6 smaller than that obtained from neutron scattering studies of other ferromagnetic metallic manganites [18] including $\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_3$ [19], $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [20], $\text{Pr}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$ [21], and $\text{La}_{0.70}\text{Pb}_{0.30}\text{MnO}_3$ [22] the first two of which are in good agreement with the measured field-dependence of $C(H)$ [15].

The low value of D from the fits to $C(H)$ can be tested in two ways. First, the parameter δ obtained from our fit to $C(T)$ at $H = 0$ yields an estimate of D , since $\delta = 0.113k_B V_{mole} \left(\frac{k_B}{D}\right)^{3/2}$ within the Heisenberg spin wave model [16]. Our value of δ corresponds to $D = 25.3 \pm 0.5 \text{ meV-}\text{\AA}^2$, in reasonable agreement with the fit to $C(H)$. Second, the very soft spin wave stiffness in the ferromagnetic state can also be tested by fitting our magnetization data, since the magnetization per unit volume at low temperatures within the Heisenberg model is given by [15,23–25],

$$M(0, H) - M(T, H) = g\mu_B \left(\frac{k_B T}{4\pi D}\right)^{3/2} f_{3/2}(g\mu_B(H - NM)/k_B T) \quad (2)$$

where $f_p(y) = \sum_{n=1}^{\infty} \frac{e^{-ny}}{n^p}$, and NM is the demagnetization field and M is the magnetization. Such a fit to $M(T)$ (shown in Figure 5 as the solid line) reproduces our data with the exception of the very lowest temperature points which are suppressed by $\sim 0.3\%$ possibly due to a minute presence of a second phase (this feature is also seen in the polycrystalline sample). A fit to the data using equation 2 yields $D = 25.1 \pm 2.1 \text{ meV-}\text{\AA}^2$ which is in agreement with our other two values.

We now discuss a possible origin of the very low ferromagnetic spin wave stiffness constant in PCMO. There is no reason to expect that the Mn-Mn ferromagnetic double exchange interaction should be a factor of 5 weaker in this compound than in all of the other ferromagnetic metallic manganites (in fact studies have shown that D at low temperatures is remarkably independent of ordering temperature in the manganites [20]), and recent neutron scattering measurements of D for the Mn spins in PCMO yield $D \sim 150 \text{ meV-}\text{\AA}^2$ [26].

While one might invoke electronic phase separation to explain the thermodynamic data, it is difficult to imagine that phase separation could reproduce quantitative agreement with the Heisenberg model consistently for the three different data sets. Furthermore, increasing the field should increase the proportion of the ferromagnetic phase which already includes ~ 90 % of the sample based on the magnetization data. Thus, for C_{mag} to decrease as strongly with field as we observe, the residual phase would need to have an associated specific heat about 100 times larger than is typical for antiferromagnetic manganites [15]. A more plausible explanation is suggested by the data of Cox *et al.* who reported that there is a ferromagnetic moment associated with the Pr ions for temperatures below $T_c = 60$ K [8]. We propose that the spin waves on this ferromagnetic sublattice are responsible for our data, and we suggest that the Pr magnetism could be critical to the low temperature thermodynamics of PCMO. Softer spin waves associated with the Pr moment would have a much larger associated specific heat than the Mn spins and therefore would dominate both $C_{mag}(T)$ and $C(H)$. A careful examination of $M(T)$ for our samples at low fields shows a distinct rise at $T \sim 50$ -60 K (Figure 5 inset), and $C(T)$ also shows a peak there, confirming the existence of the ordering transition [14]. Furthermore, in all studies of the magnetization of PCMO, the saturation moment at high fields and low temperature [6,27,28] is at least 10% higher than that of other ferromagnets, such as $\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_3$ and $\text{La}_{0.70}\text{Ca}_{0.30}\text{MnO}_3$ [25,28]. An additional ferromagnetic moment such as that from the Pr is required to explain this excess magnetization since the Mn spins in PCMO display considerable canting even at high field [3].

The ferromagnetism among the Pr ions also appears to affect the remarkable phase behavior of this material, since the ferromagnetic $T_c \sim 60$ K for the Pr corresponds to the temperature below which the field-induced and pressure-induced CAFM-FM transitions become irreversible. Furthermore, this is also the temperature above which the x-ray induced metallicity is quenched [10]. It thus appears that the Pr ferromagnetism destabilizes the CAFM phase relative to the FM phase, so that in zero field the CAFM phase is stable for $T > 60$ K but then becomes unstable to the FM phase below $T \sim 60$ K when the Pr spins order.

The free energy difference between the CAFM and FM state in zero field could be small enough that the FM state does not nucleate spontaneously at such low temperatures, but an applied magnetic field would make the FM state energetically more favorable and induce the first order phase transition. In this scenario, both the Pr ferromagnetism and its coupling to the Mn moments are crucial to understanding the physics and are therefore inseparable from the numerous unique phenomena observed in PCMO [7–11]. The importance of rare-earth magnetism to the explanation of the unusual properties of the manganites has been largely ignored in previous studies, and at least in the case of PCMO it appears that this assumption is not justified.

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FIGURES

FIG. 1. Zero-field cooled magnetization of PCMO as a function of field at $T = 10$ K. The solid line is the initial sweep up in field, the open circles and the dotted line show the subsequent field sweeps down and up respectively. The inset shows the low temperature field-temperature phase diagram [5] where the shaded region indicates the history dependent region.

FIG. 2. Magnetocaloric measurement of PCMO, showing the power, $P(H)$, required to maintain the temperature of the calorimeter at $T = 9.000 \pm 0.025$ while the surrounding cryostat was at 7.5 K. The data were taken after the sample was zero-field-cooled and the field was changed from $0 \rightarrow 9$ T (solid line), 9 T \rightarrow -9 T (dashed line), and -9 T \rightarrow 9 T (dotted line) at the rate of 6 gauss/sec (only $H > 0$ data are shown). The inset illustrates the temperature rise of the calorimeter upon the initial sweep up in the field when it is not temperature controlled.

FIG. 3. Specific heat as a function of temperature in the FM state as described in the text, $H = 0$ (open circle), $H = 3$ T (open down-triangle), $H = 6$ T (open up-triangle) and $H = 9$ T (open square). The solid lines are fits as discussed in the text. The inset shows the magnetic specific heat of the FM state at $H = 0$ and 9 T on a log-log scale. The solid lines have slope of 1.5, the dashed and the dotted lines have slopes of 2 and 1 respectively.

FIG. 4. Zero field-cooled $C(H)$, when the field is initially swept from $0 \rightarrow 9$ T (closed circles), 9 T \rightarrow -9 T (open circles) and -9 T \rightarrow 9 T (open triangles) at $T = 5.5$ K. The solid lines are the fits to the data as discussed in the text. The dotted line shows $C(H)$ for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with a constant offset to match $C(H = 0)$ for PCMO.

FIG. 5. The low temperature magnetization of PCMO as a function of temperature at $H = 7$ T. The left inset illustrates the weighted fit for the calculation of D as discussed in the text. The right inset illustrates an additional feature in $M(T)$ at low temperatures ($T < 60$ K) presumably associated with Pr ordering, where the straight line is a guide to the eye.

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